Synthesis and structures of nickel(II) trimethylacetate dimers with coordinated diamines

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Thermal decomposition of the tetranuclear nickel(II) complex $Ni_4[\eta^2\text{-}o\text{-}(NH_2)(NHPh)C_6H_4]_2(MeCN)_2(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2$ (**1**) under an inert atmosphere (*o*-xylene, 140 °C) was investigated. Under these conditions, the asymmetric binuclear complex $Ni_2[\eta^2\text{-}o\text{-}(NH_2)(NHPh)C_6H_4][(\eta^1\text{-}o\text{-}(NH_2)(NHPh)C_6H_4](\eta^2,\mu\text{-}O,O\text{-}OOCCMe_3)(\mu\text{-}O,O'\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)$ (**2**) was formed at the first stage. Complex **2** was converted into the symmetric dimer $Ni_2[\eta^1\text{-}o\text{-}(NH_2)(NHPh)C_6H_4]_2(\mu\text{-}OOCCMe_3)_4$ (**3**) upon recrystallization from benzene. The structures of complexes **2** and **3** were established by X-ray diffraction analysis.

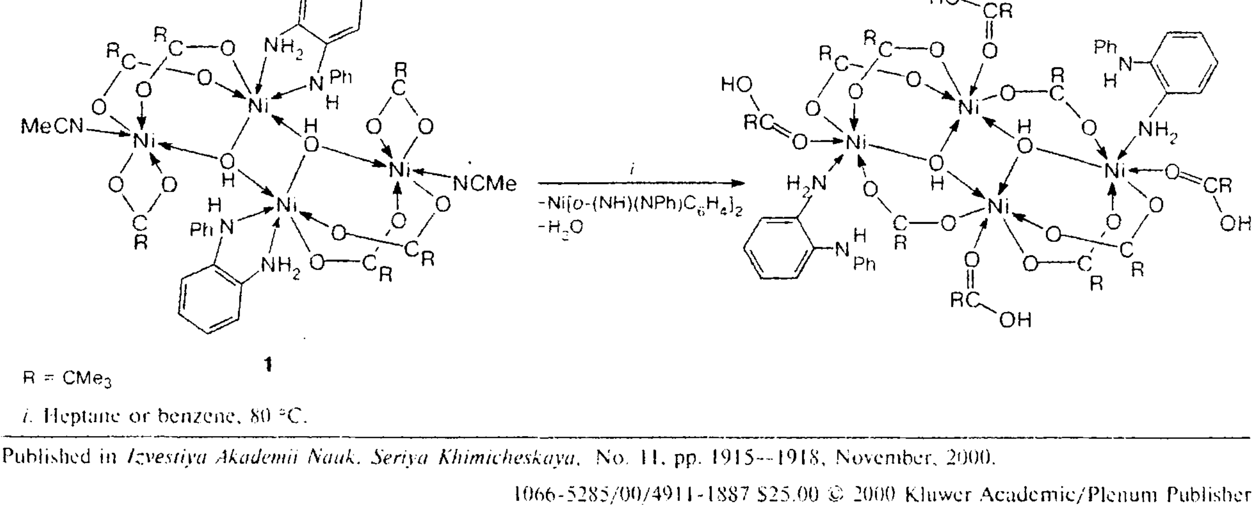
Key words: carboxylate complexes of nickel, synthesis, structure, magnetic properties.

In recent years, the chemical design of carboxylate complexes of transition metals with particular structures has acquired great importance because these compounds can serve as models of metalloenzymes or as good starting reagents for preparing new materials.[1,2] However, this problem is often difficult to solve due to the complexity of chemical mechanisms of formation of carboxylate complexes. Only recently, we have developed a versatile procedure for the preparation of nickel dimers with the "China-lantern" structure, *viz.*, $Ni_2L_2(OOCCMe_3)_4$, where L is pyridine or its substituted derivatives.[3] However, the reactions of nickel triacetates with 1,2-diamines instead of pyridine derivatives proceed according to a different mechanism to form tetranuclear hydroxocarboxylate complexes or monomers.[4,5] In the present work, we synthesized Ni^{II} dimers containing trimethylacetate bridges and monodentate-coordinated diamine ligands.

Results and Discussion

Recently, we have demonstrated that thermolysis of the complex $Ni_4[\eta^2\text{-}o\text{-}(NH_2)(NHPh)C_6H_4]_2(MeCN)_2(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2$ (**1**) in nonpolar solvents (heptane or benzene) in air (80 °C) resulted in partial oxidation of the coordinated diamine molecules to form the semiquinonediimine monomer $Ni[o\text{-}(NH)(NPh)C_6H_4]_2$ and water. In this case, another tetranuclear complex, *viz.*, $L_2Ni_4(\mu_3\text{-}OH)_2(HOOCCMe_3)_4(\mu\text{-}OOCCMe_3)_6$ (L = $o\text{-}(NH_2)(NHPh)C_6H_4$), was also obtained (Scheme 1).[6]

Scheme 1



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R = CMe$_3$

i. Heptane or benzene, 80 °C.

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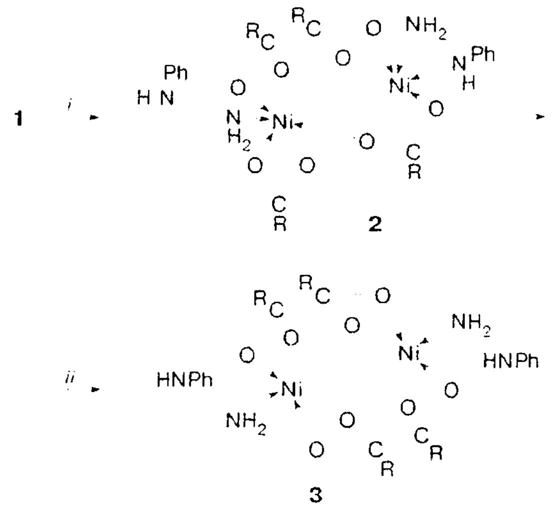
Scheme 2



R = CMe_3

i. Xylene, Ar, 140 °C; *ii.* recrystallization from benzene.

It was found that pyrolysis of complex **1** in xylene under an inert atmosphere (140 °C) did not lead to oxidation of diamine; instead, the coordinated acetonitrile molecules were eliminated and the tetranuclear core underwent destruction to form the asymmetric binuclear complex $Ni_2[\eta^2\text{-}o\text{-}(NH_2)(NHPh)C_6H_4][\eta^1\text{-}o\text{-}(NH_2)(NHPh)C_6H_4](\eta^2,\mu\text{-}O,O\text{-}OOCCMe_3)(\mu\text{-}O,O'\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)$ (**2**) (Scheme 2). It should be noted that complex **2** was not the only reaction product (the yield of the complex was 28%). Apparently, thermolysis of complex **1** was accompanied by the formation of other compounds, which we failed to isolate and characterize.

Table 1. Principal bond lengths (*d*) and magnetic properties of binuclear nickel trimethylacetates **2** and **3**

Parameter	Complex **2**	Complex **3**
d/Å		
Ni...Ni	3.394(4)	2.4967(4)
Ni—O($OOCR_{bridge}$)	1.967(9)— —2.000(9)	1.989(1)— —2.038(1)
Ni—O($OOCR_{chelate\text{-}bridge}$)	2.066(8)— —2.094(8)	—
Ni—O($OOCR_{chelate}$)	2×2.091(8)	—
Ni—N(NH_2)	2.168(11), 2.087(10)	2.038(1)
Ni—N(NPhH)	2.142(10)	—
N(NH_2)—C(C_6H_4)	1.44(2), 1.42(2)	1.435(2)
N(NPhH)—C(C_6H_4)	1.43(2), 1.49(2)	1.404(2)
N—C(Ph)	1.37(2), 1.467(2)	1.399(2)
μ_{eff}(296—77 K)/μB	2.65—1.87	2.12—0.87

According to the X-ray diffraction data, the nickel(II) atoms in complex **2** are separated by a nonbonded distance (3.394(4) Å). The metal atoms are linked *via* two bridging carboxylate groups (Ni—O, 1.967(9)—2.000(9) Å; C—O, 1.22(2)—1.30(2) Å; the O—C—O angles are in the range of 125.0(1)—125.7(1)°) and one chelate-bridging carboxylate group (Ni—O, 2.066(8)—2.094(8) Å; C—O, 1.29(2) Å; the O—C—O angle is 117.9(1)°) (Fig. 1, Table 1). One oxygen atom of the latter group is coordinated to both nickel atoms, whereas the second O atom of this carboxylate group is coordinated to only one of the Ni atoms (Ni—O, 2.199(8) Å). The fourth carboxylate group is coordinated to the other

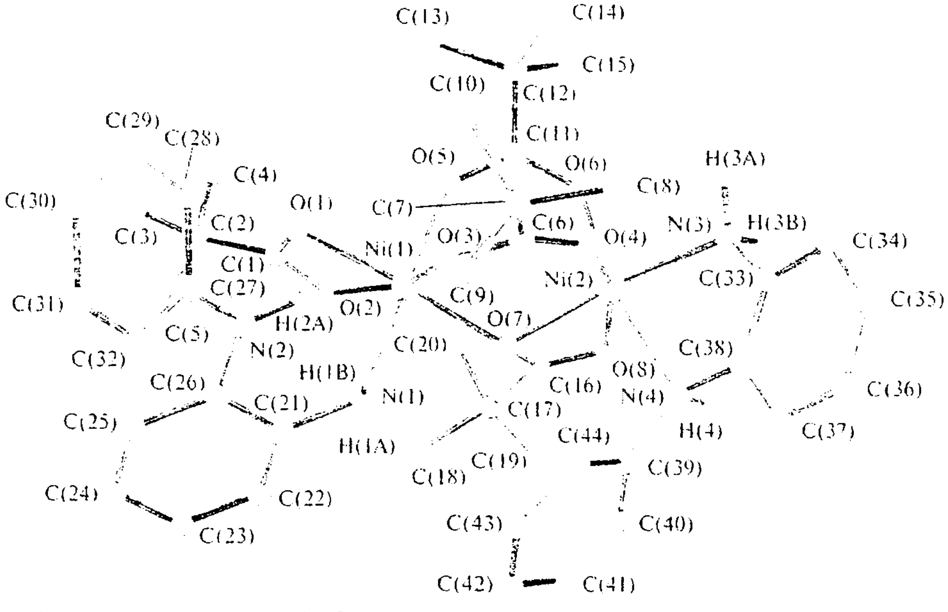


Fig. 1. Structure of asymmetric dimeric complex **2**.

metal atom in a chelate form (Ni—O, 2×2.091(8) Å; C—O, 1.26(2) and 1.29(2) Å; the O—C—O angle is 118.3(1)°). The coordination sphere about this nickel atom is completed with the nitrogen atom of the NH_2 group of the monodentate-coordinated diamine ligand (Ni—N, 2.168(11) Å). The second diamine molecule is chelate-bonded (Ni—N(NH_2), 2.087(10) Å; Ni—N(NPhH), 2.142(10) Å) and is coordinated to the opposite metal center. As a result, both Ni^{II} atoms are in an octahedral environment and have 20-electron configurations.

After recrystallization from benzene, complex **2** was converted into the symmetric dimer $Ni_2[(\eta^1\text{-}o\text{-}(NH_2)(NHPh)C_6H_4]_2(\mu\text{-}OOCCMe_3)_4$ (**3**) (see Scheme 2). According to the X-ray diffraction data (Fig. 2, see Table 1), an extremely short Ni...Ni distance (2.4967(4) Å) is observed in molecule **3** (up to now, the shortest known Ni—Ni distance in this type of complexes was 2.609 Å; it has been found by us previously in the pyridine derivative).[3] In spite of this fact, a direct metal—metal bond in molecule **3** is absent and the complex is antiferromagnetic (see Table 1).

In general, complex **3** has a typical "dimeric lantern" structure and contains four virtually equivalent carboxylate bridges (Ni—O, 1.989(1)—2.038(1) Å; C—O, 1.255(2)—1.260(2) Å; the O—C—O angles are 124.3(1) and 124.4(1)°) and two apical monodentate diamine ligands linked through the more rigid NH_2 group (Ni—N, 2.038(1) Å; the N—Ni...Ni angle is 177.55(4)°).

To summarize, the conversion path, *viz.*, a trimethylacetate nickel-containing polymer (the major initial product) → tetramer **1**[5] → a tetramer → an asymmetric dimer → a dimer with the "lantern" structure, gives promise that the directed synthesis of such structures containing diamine ligands may be performed.

Experimental

The synthesis of new complexes was carried out under an atmosphere of pure argon with the use of anhydrous solvents prepared according to standard procedures. The starting tetramer $Ni_4[\eta^2\text{-}o\text{-}(NH_2)(NHPh)C_6H_4]_2(MeCN)_2(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2$ (**1**) was synthesized according to a known procedure.[5] The IR spectra were recorded on a Specord M80 instrument in KBr pellets. The static magnetic susceptibilities χ'_m were measured using the Faraday method in the temperature range of 77—300 K with an instrument at the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.[7] The effective magnetic moments were calculated according to the following formula:

$$\mu_{eff} = (8\chi'_M T)^{1/2}.$$

Synthesis of the complex $Ni_2[(\eta^2\text{-}o\text{-}(NH_2)(NHPh)C_6H_4][(\eta^1\text{-}o\text{-}(NH_2)(NHPh)C_6H_4](\eta^2,\mu\text{-}O,O\text{-}OOCCMe_3)(\mu\text{-}O,O'\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)$ (2). A pale-green solution of tetramer **1** (1 g, 0.80 mmol) in *o*-xylene (25 mL) was refluxed for 1 h. The resulting brown-green solution was concentrated to 5 mL. Then an equal amount of anhydrous hexane was added and the reaction mixture was kept at −5 °C for one day. Heating of the solution to ~20 °C followed by storage over a short period at this temperature afforded pale-green crystals of complex **2** suitable for X-ray diffraction analysis. The yield was 0.4 g (28%). Found (%): C, 59.9; H, 6.5; N, 6.5. $C_{44}H_{60}N_4Ni_2O_8$. Calculated (%): C, 59.35; H, 6.79; N, 6.29. IR, ν/cm⁻¹: 3352 m, 3334 m, 3320 m, 3246 m, 3048 w, 2960 m, 2936 m, 2864 w, 1664 s, 1600 v.s, 1585 s, 1498 s, 1440 s, 1456 m, 1416 s, 1360 s, 1296 m, 1224 m, 1208 m, 1080 s, 1016 s, 880 w, 792 s, 744 v.s, 696 v.s, 608 m, 756 w, 544 w, 488 m, 416 m.

Synthesis of the complex $Ni_2[(\eta^1\text{-}o\text{-}C_6H_4(NH_2)(NHPh)]_2(\mu\text{-}OOCCMe_3)_4$ (3). Recrystallization of complex **2** (0.23 g) from benzene (25 mL) afforded green crystals of compound **3** as a solvate with a benzene molecule in a yield of 0.20 g (87%). Found (%): C, 62.3; H, 6.6; N, 5.9.

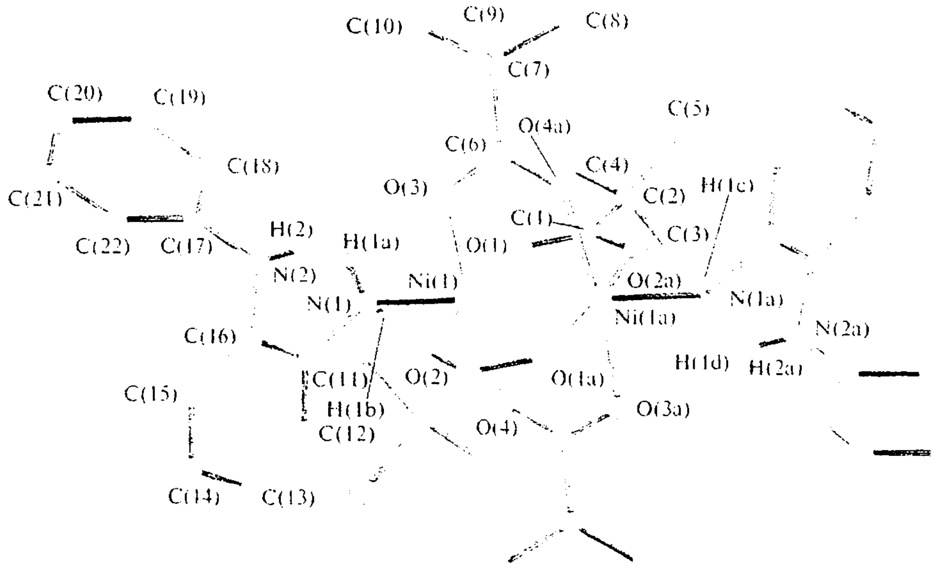


Fig. 2. Structure of dimeric complex **3** with the "China-lantern" structure.

Table 2. Crystallographic parameters of carboxylate complexes **2** and **3** · C_6H_6

Parameter	**2**	**3** · C_6H_6
Molecular formula	$C_{44}H_{60}N_4Ni_2O_8$	$C_{50}H_{66}N_4Ni_2O_8$
Space group	*Pbcn*	$P\bar{1}$
a/Å	25.758(7)	9.247(1)
b/Å	16.832(4)	11.665(2)
c/Å	24.551(7)	12.553(2)
α/deg	90	91.594(3)
β/deg	90	107.717(3)
γ/deg	90	107.632(3)
V/Å^3	10645(5)	1218.4(3)
Z	8	1*
ρ_{calc}/g cm^{-3}	1.111	1.309
μ/cm^{-1}	0.753	0.824
Radiation	Mo-Kα (λ = 0.71073 Å)	
θ-2θ scanning range/deg	3—60	2—60
Number of independent reflections	6527	6104
Number of reflections with $I > 4\sigma$	4255	5782
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.1344F^2$	Unit weights
R_1	0.0921	0.0334
wR_2	0.1822	0.0935

* The molecule is located in the crystallographic inversion center.

$C_{50}H_{66}N_4Ni_2O_8$. Calculated (%): C, 62.01; H, 6.87; N, 5.78. IR-, ν/cm^{-1}: 3344 m, 3256 m, 2960 m, 2928 m, 2864 w, 1672 w, 1608 v.s, 1592 v.s, 1496 s, 1480 s, 1424 s, 1376 m, 1360 m, 1304 m, 1246 w, 1224 m, 1056 s, 880 m, 800 m, 774 v.s, 696 s, 680 m, 648 w, 616 m, 576 m, 448 m, 464 w, 440 w.

X-ray diffraction study. Crystals of complexes **2** and **3** suitable for X-ray diffraction study were prepared as described above. The X-ray intensity data sets were collected on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.[8] The semiempirical absorption correction was applied.[9] The crystallographic parameters and selected details of the refinement of both structures are given in Table 2.

The structures of both complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands and the phenyl rings of the coordinated diamine molecules were calculated geometrically and refined using the riding model. The positions of the hydrogen atoms of the NH and NH_2 groups of the ligands were located from difference Fourier syntheses and refined isotropically. All calculations were carried out with the use of the SHELX97 program package.[10] The main geometric parameters of the complexes are given in Table 1.

X-ray diffraction analysis was performed in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences).

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